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## Photoelectron studies of machined brass surfaces

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UV photoelectron spectroscopy has been used to determine the surface composition of machined brass. The results show a considerable change between the photoelectron surface composition and the bulk composition of the same sample determined by energy-dispersive X-ray fluorescence. On the surface the lead composition is increased by ~900%. This is consistent with the important part that lead is believed to play in improving the machinability of this alloy.

### 1. Introduction

It is generally assumed that the element lead is added to brass to improve the machining properties of the alloy [1]. The improved machining property is due to the action of lead forming a thin surface layer and acting as a lubricant during the cutting process.

The technique of UV photoelectron spectroscopy is known to be highly surface-sensitive producing chemical and elemental information on the structure of the first few atomic layers of a solid. It should therefore be an ideal technique to provide information on the surface composition of machined brass and of any changes in the surface composition compared to that of the bulk [2]. Brass is a particularly suitable candidate for compositional study by UV photoelectron spectroscopy since the three elemental constituents Cu, Zn and Pb each possess  $d^{10}$  subshells which do not overlap and are energetically within the He II (40.8 eV) photon energy range. Photoelectron features from these shells can therefore be used to infer the elemental composition of the surface. In order to provide a clean metal surface required for photoelectron spectroscopy it is necessary to remove the contaminated surface layers (oxides or "carbon") under the UHV conditions

required for surface studies. Techniques such as Ar ion bombardment are normally used for this purpose. Unfortunately, such cleaning procedures while removing contamination can also affect the composition of the metal surface giving rise to spectra which may not be characteristic of the original surface. To overcome this problem we have made use of a vacuum lathe-photoelectron spectrometer in which the surface of a freshly machined target can be examined without resort to further surface cleaning. The composition of the surface deduced from photoelectron measurement can then be compared with that deduced by X-ray fluorescence measurements obtained using a scanning electron microscope. This technique is far less surface-sensitive, the sampling depth for brass being around 1  $\mu\text{m}$  and the composition corresponding to that of the bulk material.

### 2. Experimental

The vacuum lathe-photoelectron spectrometer used in these experiments was essentially similar to the one described previously [3] with the exception that the current spectrometer is controlled by a microcomputer so that spectra can be

stored for processing later. The lathe operates at a vacuum of between  $1 \times 10^{-6}$  and  $1 \times 10^{-5}$  mbar, the target rod being rotated at between 1 and 10 rps. The sample rod is irradiated by He I/II radiation from a hollow cathode discharge approximately half a rotation after it has been machined clean by a tungsten carbide cutting tool. Photoelectrons ejected at  $90^\circ$  to the photon beam are then energy-analysed by a  $150^\circ$  spherical sector electrostatic energy analyser (fig. 1) and used to generate a UV photoelectron spectrum. The short time interval between the metal surface being cleaned and sampled by the UV photons means that the machined surface is only exposed to between 0.05 and 5.0 L of background gas before being studied. Spectra are therefore consistent with clean metal spectra recorded under UHV conditions even though they are obtained with a HV apparatus [3]. Standard samples of commercial high-speed machining brass rod (type CZ121 4Pb) were used and turned into suitable rods (6.0 mm diameter) for mounting in the vacuum lathe. Rod samples of the constituent elements were also prepared and examined with the photoelectron spectrometer. These samples were also examined by X-ray fluorescence.

The X-ray fluorescence studies were carried out on a JEOL JEM T100 scanning electron microscope using a Link AN10000 energy-dispersive X-ray fluorescence analyser. Quantitative elemental analysis of the samples was performed

using Link ZAF4/FLS software<sup>††</sup> which is suitable for the analysis of flat surfaces. An elemental analysis was carried out on a brass rod (type CZ121 4Pb) with its end machined flat and upon a section of brass sheet (type CZ108) polished with diamond abrasive to a  $0.25 \mu\text{m}$  finish. This second analysis was carried out because it is known that sheet brass contains negligible lead. To improve the accuracy of our composition determinations, spectra of the constituent elements were recorded and included as standards within the Link Analytical software package. Such a procedure should lead to an accuracy of between 1% and 2%.

### 3. Results and discussion

The He I/II photoelectron spectra of machined brass rod and of the constituent elements are shown in fig. 2. The assignments follow from published spectra of the polycrystalline elements [3,4] and are indicated in the figure. The analysis will be confined to those features corresponding to ionization by the He II (40.8 eV) line and particularly to the Zn 3d and Cu 3d features and the Pb 5d feature. These features are not overlapped and hence areas can be measured accurately and used to deduce the proportion of the elements on the surface. Since the electron energies involved are all greater than 16 eV and the analyser voltages are scanned to produce spectra, the transmission function for the spectrometer for these features should simply be proportional to electron energy if band areas are considered. Thus the intensities of the d-shell features corrected for transmission function will simply be proportional to the band area divided by the corresponding electron energy. From fig. 2 it is clear that as far as the spectra are concerned the alloy can be considered essentially as a mixture of the constituent elements. Thus although minor variations between the 3d density of states for metallic copper and alloyed copper are indicated

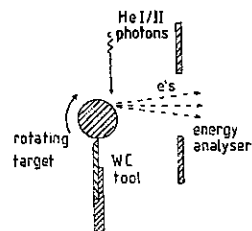


Fig. 1. Outline drawing of vacuum lathe-photoelectron spectrometer.

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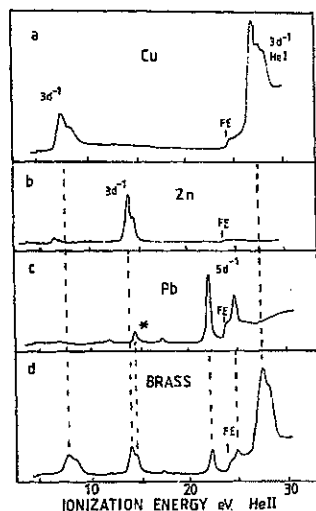


Fig. 2. He II photoelectron spectra of machining brass and its constituent elements. (HeI features are indicated on the spectra, FE are He I Fermi edge features and \* indicates Pb 5d<sup>-1</sup> ionization on the He II 48.4 eV line. A small contribution from this feature to the brass Zn 3d<sup>-1</sup> feature is allowed for in intensity calculations.)

in spectra 2a and 2d, spectrum 2d – the photoelectron spectrum for brass – can be largely represented as a linear sum of spectra 2a to 2c. It should thus be possible to use the information in spectrum 2d to obtain an estimate of the surface composition of machined brass. To do this it is necessary to know not only how the transmission function of the spectrometer varies over the electron energy range of interest but also the photoionization cross-sections for the particular elemental subshells at the He II energy. It is also assumed that the sampling depth, that is the electron mean free path, remains essentially constant over the limited electron energy range of

interest [2]. Since experimental photoionization cross-sections are not available we have used the comprehensive compilation of Yeh and Lindau obtained by Hartree-Fock-Slater calculations [5]. An allowance for the asymmetry in the photoelectron emission on intensity has also been made using Yeh and Lindau's data. One-electron calculations of UV photoionization cross-sections are known to be inadequate because of their inability to include electron correlation effects [6]. However, it is assumed here that use of these cross-sections will produce at least a qualitatively correct proportional composition. It is recognised that the accuracy of the composition deduced could be improved should either better calculations or experimental photoionisation cross-section measurements become available. Thus if  $A$  is the measured band area corresponding to an electron kinetic energy  $E$  and  $\theta$  is the He II photoionization cross-section for 90° photoemission, the reduced band intensity  $I$  is given by the relationship:

$$I = A / (\theta \times E).$$

$I$  is then proportional to the number of atoms of a particular element on the surface. From the above considerations it is possible to use spectrum 2d to give the proportional elemental composition and this is given as the percentage elemental composition in table 1. These results are the average of four separate determinations and correspond to the transmission corrected, relative

Table 1  
Percentage elemental composition of brass

Measurement	%Cu	%Zn	%Pb
A	33	53	14
B	59.6	38.9	1.5
C	59.8	38.9	1.3
D	64.9	35.0	0.15
E	64.3	35.6	0.1

A: Photoelectron determination of the surface composition of machined brass rod.

B: X-ray fluorescence determination of the composition of machined brass rod.

C: Manufacturers stated composition of brass rod.

D: X-ray fluorescence determination of the composition of brass sheet.

E: Manufacturers stated composition of brass sheet.

intensities of 24:27:43 for Cu:Zn:Pb. The statistics of the experiment lead to an error of  $\pm 2$  in the quoted percentage composition. However, as already indicated, this ignores any uncertainties introduced by the use of theoretical photoionization cross-sections. Also given in table 1 are the percentage elemental compositions of rod and sheet brass determined by X-ray fluorescence and compositions given in commercial tables for the particular types of brass used.

It is immediately obvious that good agreement exists between the X-ray fluorescence results and the bulk composition published for brass alloys. From the bulk point of view brass rod contains 58.6% Cu, 38.9% Zn and only 1.5% Pb to improve the machinability while for sheet brass the proportion of Pb falls to 0.15%. For the photoelectron measurements however, which reflect particularly the surface composition, there is approximately a ninefold increase in the percentage composition of lead, indicating the important part played by a "trace" of this element in determining the machining properties of the alloy. The proportion of Zn on the surface is also considerably increased (53%) compared to the bulk while the surface composition of copper is decreased (33%) with respect to the bulk. These changes will be important in establishing the surface properties of the machined alloy and in determining its machining properties. They may perhaps be understood qualitatively in terms of the variations of Young's modulus for the elements, i.e. Cu 1.23, Zn 0.9 and Pb 0.16 ( $\times 10^{11}$  N m<sup>-2</sup>) [1]. Although it would be invalid to transfer these values to the alloy situation it is clear that the ease of deformation for a given stress will be Pb > Zn > Cu suggesting that lead will be most easily "spread" on the surface and that the surface concentration of Zn might also be enhanced in this way although to a much lesser extent. It would appear that the surface enhancement process is purely mechanical, the lead acting as a simple lubricant being retained on the surface rather than removed in turnings. Such a process would allow a small concentration of lead atoms trapped at grain boundaries within the bulk to rapidly become concentrated at the metal surface. An alternative mechanism that might be

considered would be surface segregation of lead atoms by diffusion. However, models of this process in the recent literature indicate that even assuming that the temperature at the cutter might be somewhat above ambient, the time available between successive passes of the machining blade (< 1 s) would be insufficient for substantial diffusion of lead atoms to the surface to take place [7]. This process would also be difficult to support since it would lead to selective removal of lead from the alloy which should lead to a gradual reduction of the observed lead concentration. No such effect was observed.

It would clearly be of interest to obtain in addition to the X-ray fluorescence (bulk) composition and machined UPS (surface) composition a UPS study of the clean alloy surface without machining. This would require use of a UHV spectrometer to which we do not currently have access. However, such a study would require that the alloy surface should be cleaned. Ar-ion bombardment is the standard method of surface cleaning but this process is known to be selective and for alloys to result in surface compositions not representative of the bulk material [8–10]. Because of the volatile nature of zinc, annealing, which is the normal procedure used to compensate for changes in surface composition introduced by Ar-ion bombardment, is not an acceptable method of surface preparation for brass since it causes Zn depletion at the surface. To overcome these problems, sample scraping has been used for UPS studies of brass [10]. Our results indicate that such an approach must be applied with care when the relative intensities of features in the spectrum are of importance. These considerations indicate that it would probably be difficult to obtain a reliable UPS spectrum of a clean non-machined brass surface even in a UHV spectrometer.

#### 4. Conclusions

He II UPS spectra of machined brass are presented, obtained using a combination of a vacuum lathe and a photoelectron spectrometer. The spectra are interpreted in terms of the elemental

surface composition of the machined alloy. The results indicate that compared with the bulk composition determined by X-ray fluorescence spectroscopy the lead composition of the surface layer is considerably enhanced. The results are consistent with a simple mechanical mechanism whereby lead is retained on the surface and acts as a lubricant in the machining process.

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# Surface Composition of Machined Lead Brass

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ESCA and RBS were used to obtain quantitative information on the thickness and nature of the surface layers formed on machined brasses containing 1–3% lead. The results show that the brass surface is strongly enriched in lead. The amount of this element accumulated on the surface increases with increasing bulk concentration. Lead appears to be present as islands partially covering the brass surface and having variable thicknesses up to several hundred Å. The outermost layer of the islands is mainly a Pb hydroxycarbonate, under which PbO and Pb metal can be detected. Between the islands, the brass surface is covered by a layer of zinc oxide covering the Cu–Zn metallic phase. The accumulation of Pb at the surface is attributable to a smearing effect caused by the machining tool.

## INTRODUCTION

Brass containing a small percentage of lead has been widely used in the production of components for plumbing devices because of its better machinability. The machining process appears, however, to cause an accumulation of lead at the brass surface. Since recent environmental regulations of some countries have restricted the maximum contamination level allowed for lead in potable water, new emphasis has been devoted to studies in plumbosolvency from a machined surface of leaded brass and in mapping its morphology in order to obtain a better understanding of the interaction with water and to prevent lead release.

The aim of our work was to obtain quantitative information on the amount of lead accumulated at the brass surface after machining, and on the thickness and nature of the surface layer using ESCA. Since we found that the thickness of the lead layer may exceed the depth range explored by ESCA, Rutherford backscattering spectroscopy (RBS) was also used on some samples to obtain information on the Pb thickness distribution.

A study on the surface composition of machined brass using photoelectron spectroscopy has recently been reported.<sup>1</sup> In that work, the authors, using UV photoemission from the 3d subshells of Cu, Zn and Pb, found an increase by a factor of about ten in the lead composition at the surface compared to the bulk. Because the surface examined was machined under vacuum, there is still a lack of information on the composition and chemical state of the surface layer upon machining in air.

## EXPERIMENTAL

The samples examined were all brasses with a typical composition around Cu 60% by weight, with Pb contents varying between 1 and 3% and minor amounts of other metals, as reported in Table 1. They were specially prepared by the Research Centre of Europa Metalli-LMI Spa with a semicontinuous casting, starting from pure metals. Their compositions are typical of commercial leaded brasses.

The machining of the sample surfaces was performed with a lathe in dry conditions with a speed of 600 rpm, a material feed of 0.075 mm/turn and a cutting deepness of 0.5 mm, using a new tool for each sample. The tools used were Mitsubishi inserts HT10 TCMW16T304. The final shape of these samples was cylindrical with 38 mm diameter, corresponding to a linear tool speed of 1.2 m s<sup>-1</sup>.

The XPS spectra were obtained in a Vacuum Science Workshop ESCA instrument, using Al or Mg K $\alpha$  radiations. The binding energy (BE) scale was calibrated on the Cu 2p<sub>3/2</sub> and Cu 3p peaks for metallic copper, assuming the literature values of 932.7 and 75.1 eV, respectively.<sup>2</sup>

The samples were introduced into the analysis chamber as received after the dry machining process, without any

Table 1. Bulk composition of the samples (weight%). Minor impurities not included

Sample	Cu%	Zn%	Pb%	Ni%	Sn%	Fe%
S1	59.83	39.0	1.07	0.030	0.01	0.02
S2	59.67	38.8	1.43	0.046	0.01	0.02
S3	58.50	39.0	2.48	0.023	0.01	0.02
S4	59.08	37.9	2.93	0.020	0.01	0.02

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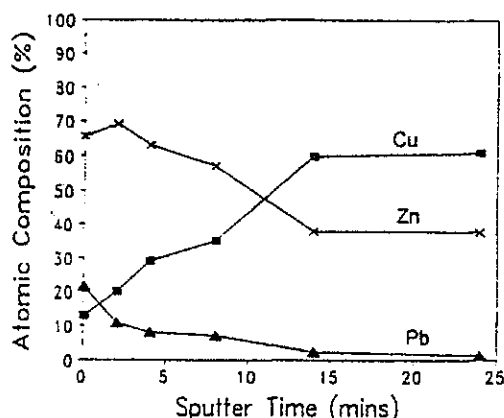


Figure 1. XPS depth profile of a brass sample containing 1.2% lead in the bulk, obtained by ion bombardment with 2 KeV  $\text{Ar}^+$  ions.

treatment. At first, the approximate surface composition (at.%) was determined using the atomic sensitivity factors reported in Ref. 2. The chemical states of the elements were attributed by comparison with the XPS spectra obtained in our instrument for the compounds Cu,  $\text{Cu}_2\text{O}$ , Zn, ZnO, Pb, PbO and  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  (lead hydroxycarbonate). The non-metallic samples were powders supported on adhesive tape. For them, the energy scale was calibrated using a BE of 285.0 eV for contamination C 1s. In the case of the metallic samples, including our brasses, we found no evidence of any significant charging of the surface oxide layers.

Lead hydroxycarbonate can be identified on the basis of the BE of Pb  $4f_{7/2}$  (139.0 eV), the O 1s structure (a broad band centred around 532 eV due to  $\text{CO}_3$  and OH groups), the presence of a C 1s component characteristic of  $\text{CO}_3$  (289.5 eV) and the ratios Pb:C:O; it was found to be present as a thin layer covering the oxide formed on the surface of lead metal cleaned under a vacuum and exposed to air.<sup>3</sup>

Since the Zn 3s line overlaps the Pb 4f doublet, the peak area of Pb 4f was corrected by subtracting 40% of the Zn 3p peak area from the sum of the Pb 4f + Zn 3s. Since the Zn 3s line is rather weak, this correction was significant only when Pb was present in very small amounts.

In order to obtain information on the variation of the surface composition in depth, XPS depth profiling was performed on some samples by sputtering with 2 keV  $\text{He}^+$  ions, using a beam current of about 4  $\mu\text{A}$  rastered over a surface of about  $15 \times 15$  mm.

The RBS results were obtained with a single ended Van de Graaff accelerator model KN300 working with 2 MeV  $\text{He}^+$  ions and a scattering angle of  $135^\circ$ .

## RESULTS AND DISCUSSION

The surface compositions are listed in Table 2. They were obtained using the intensities of the Cu  $2p_{3/2}$ , Zn  $2p_{3/2}$  and Pb 4f. Using higher kinetic energy (keV) peaks for Cu and Zn, having higher escaping depths, different compositions were found, thus indicating that the elemental concentrations vary significantly with the

Table 2. Surface composition determined by XPS (at.%) (carbon not included)

Sample	Cu	Zn	Pb	O
S1	5.0	22.2	9.6	63.1
S2	5.3	23.2	9.5	62.0
S3	3.7	18.2	13.6	64.5
S4	3.5	17.1	15.0	64.4

depth already in the first 50 Å. According, significant variations of the relative peak intensities were observed if the spectra were recorded at higher acceptance angles from the surface normal. These variations, together with those observed upon sputtering, were taken into account in order to derive conclusions about the composition of the surface layers covering the bulk alloy. Carbon was not included in the computation of the elemental composition, since it is mainly attributable to surface contamination. However, a C 1s component at about 289.5 eV was observed on all samples and attributed to the presence of carbonate (see below).

From Tables 1 and 2 we can see that the content of lead at the surface is much higher than that in the bulk. The surface enrichment of Pb is related to its bulk concentration. The surface is also enriched in zinc.

On the basis of their 2p and Auger  $\text{L}_{3\text{M}_{45}\text{M}_{45}}$  peak positions, the chemical states of Cu and Zn can be derived. Cu is mainly in the metal state, while Zn is mainly oxidized, although a fraction of it (about 10–15%, as derived by curve-fitting its Auger peak components) is in metal form (see Fig. 2).

Lead appears to be present mainly in an oxidized form (see Fig. 3). The intensity of the  $\text{CO}_3$  component in C 1s roughly corresponds to the atomic ratio found for the compound  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  (lead hydroxycarbonate). The BE of Pb  $4f_{7/2}$  (about 139.0 eV) and the O 1s structure (a broad band centred around 532 eV, see Fig. 4) are in agreement with the presence of this compound, that was also found in separate experiments on the surface of lead exposed to air (see experimental section). In other separate experiments, we also found that zinc metal exposed to air is covered by ZnO and  $\text{Zn}(\text{OH})_2$ , but no carbonate. Thus our conclusion is that lead on the topmost surface layer in contact with air is present mainly in the form of hydroxycarbonate.

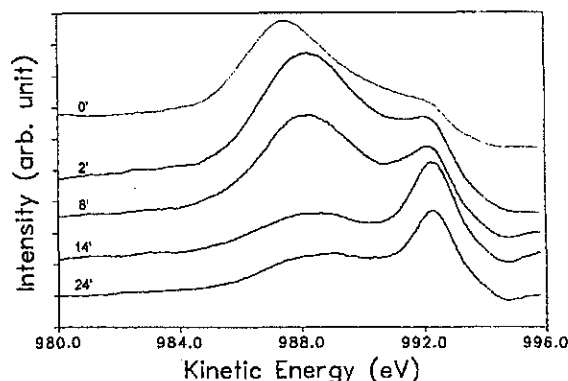


Figure 2. Variation of Zn  $\text{L}_{3\text{M}_{45}\text{M}_{45}}$  Auger peak ( $\text{Mg K}\alpha$ ) at different sputtering times (minutes). Same sample as in Fig. 1. The broad peak at lower KE is due to oxidized Zn, while the sharper one at higher KE is Zn metal.



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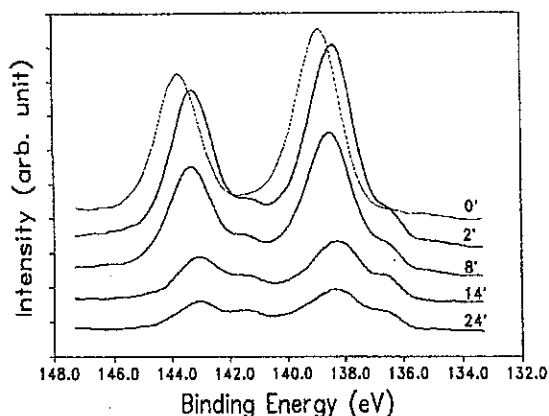


Figure 3. Variation of Pb 4f at different sputtering times (minutes).

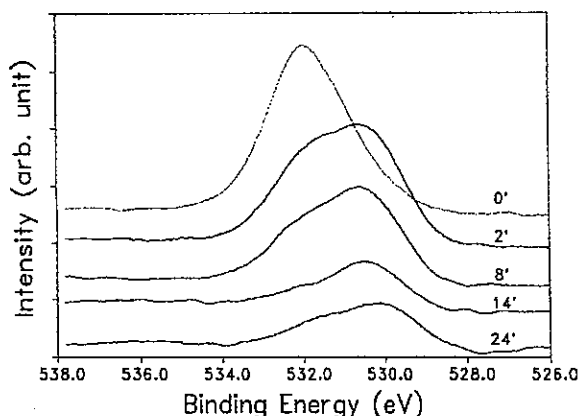


Figure 4. Variation of O 1s at different sputtering times (minutes).

In Fig. 1, the XPS depth profile of a sample containing 1.2% Pb in the bulk is shown. In Figs 2, 3 and 4 the corresponding variations of Zn  $L_{3/2}M_{4,5}M_{4,5}$  Auger, Pb 4f doublet and O 1s peaks are reported. It is clear that zinc is accumulated on the surface as oxide (KE for ZnO 988.2 eV, for Zn metal 992.1 eV) covering the Cu-Zn metal phase. The lower KE (987.4 eV) observed before sputtering seems to be attributable to a thin surface layer of zinc hydroxide.

Lead 4f<sub>7/2</sub> shows an initial shift from 138.9 (hydroxycarbonate) to 138.5 eV (PbO), while the metal component (136.8 eV) becomes more apparent. The overall decrease of the Pb signal with increasing sputtering time, indicates that the fraction of the surface covered by this element decreases, until it reaches that corresponding to the bulk, where lead is found at the grain boundaries.

In agreement with the changes of the Zn and Pb lines, the O 1s changes from a band centred around 532 eV BE (attributable to CO<sub>3</sub> and OH groups) to about 530.5 (oxides).

The depth profiles of all the samples examined were qualitatively similar. However, the thickness of the oxidized layers was found to depend on the time elapsed between the machining of the sample surface and ESCA analysis.

The above ESCA results can be interpreted if we assume that the surface of the samples after machining

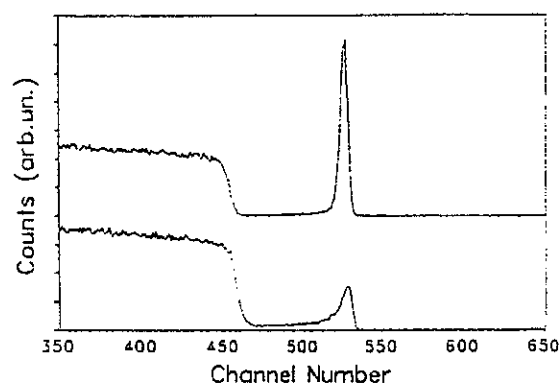


Figure 5. RBS spectra of a 100 Å gold film deposited on copper (upper curve) and of a brass sample containing 2.4% lead (lower curve).

is partially covered by Pb islands, the remaining fraction being covered by zinc oxide. If the Pb islands are considered to be thicker than the mean escape depth of the electrons, the atomic ratio between oxidized Pb and Zn corrected with their atomic densities, should make it possible to evaluate the fraction of the surface covered by the Pb islands. However, since the exact amounts of all the surface compounds are not well defined, a reliable correction for the densities is not possible, so that we can conclude that the fraction of the surface covered by the Pb islands varies from about 30 to 50% depending on the bulk content in the alloy. Their thickness cannot be derived from our XPS depth profiles, owing to lack of calibration of the sputtering rates. The gradual decrease of the Pb signal, however, indicates that the islands do not have a constant thickness, but show a distribution of thicknesses ranging up to several hundred Å.

Since lead is almost totally insoluble in the copper-zinc alloy and is found in the form of dispersed particles localized along the grain boundaries of the brass matrix, its accumulation at the surface is mainly attributable to a smearing effect caused by the machining tool. It is to be ascertained if the spreading of lead on the surface is attributable to a simple mechanical effect or is also due to the local heating caused by the tool.

In order to evaluate better the distribution of thicknesses of the Pb islands, RBS technique was employed. In Fig. 5 the spectrum of a brass sample containing 2.4% Pb is shown together with that of a 100 Å gold film deposited on copper (Au has a mass very close to that of Pb, thus it has a similar stopping power). The Pb peak in the brass spectrum is strongly asymmetric, showing a tail extending at lower energies than the surface peak. A comparison of the two spectra clearly shows the thickness distribution for lead extends up to several hundred Å. The lower intensity of the Pb signal relative to that of the alloy matrix, compared to that of the Au film, confirms that the Pb islands cover only a fraction of the brass surface, in agreement with our ESCA results.

Our results are in qualitative agreement with those reported in Ref. 1, where a strong surface enrichment in Pb was found upon machining the surface of brasses containing 1.5% Pb using a lathe operated under a vacuum of  $10^{-5}$ – $10^{-6}$  mbar. A significant enrichment in Zn was also found in Ref. 1 and was attributed, as in the case of Pb, to a mechanical effect causing a preferential

spreading of Zn with respect to Cu. In our case, the enrichment in Zn can also be attributed to the oxidation process occurring immediately after the cutting of the sample surface in air.

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## CONCLUSIONS

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The results of our ESCA analysis show that the sample surface is strongly enriched in lead. The surface layer is mainly composed of zinc and lead in an oxidized form, with a Pb/Zn atomic ratio of 0.5:1. This ratio is found to increase with increasing the Pb bulk concentration.

Lead appears to be present as islands partially covering the brass surface and having variable thicknesses up to several hundred Å. The outermost layer of the islands is mainly a Pb hydroxycarbonate, under which PbO and

Pb metal can be detected. Between the islands, the brass surface is covered by a thin layer of zinc oxide covering the Cu-Zn metallic phase.

The relatively high fraction (30–50%) of surface covered by the Pb islands is the result of a smearing effect caused by the machining tool.

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